Communication

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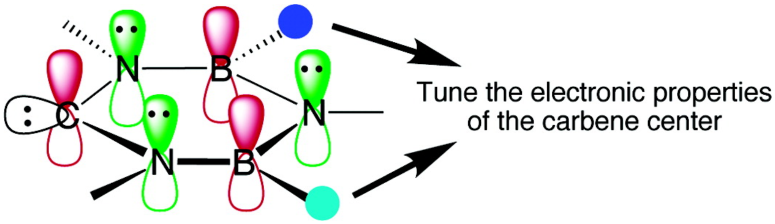

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Stable Planar Six-π-Electron Six-Membered N-Heterocyclic Carbenes with Tunable Electronic Properties

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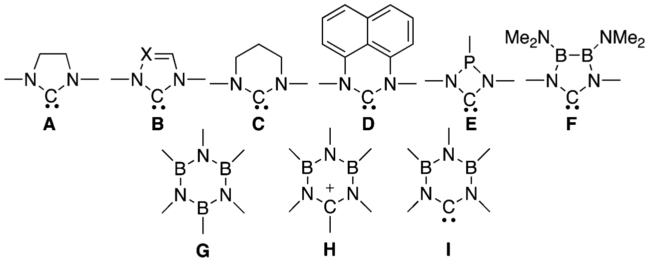
The last 15 years have seen tremendous advances in carbene chemistry that transformed these electron-deficient species[1] into the realm of isolable compounds[2] and powerful tools for synthetic chemists. Despite the existence of several families of stable carbenes, it has to be recognized that, so far, only the cyclic diamino carbenes (NHCs) have found numerous applications. NHCs are excellent catalysts on their own,[3] and there is increasing experimental evidence that NHC−metal catalysts surpass their phosphine-based counterparts in both activity and scope of application.[4] Having said that, it is clear that the success of phosphorus- and nitrogen-based ligands was, and is still, due to their enormous structural diversity. So far, the structures of stable NHCs available have been largely restricted to saturated and unsaturated five-membered heterocycles **A**[5] and **B**,[6] the only exceptions being carbenes **C**−**F**[7] (Scheme 1). Moreover, it has been shown that free acyclic carbenes, including diamino carbenes,[8] are far more fragile than NHCs and are poor ligands for transition metal complexes.[9] Therefore, it is of interest to design new stable cyclic diamino carbenes possessing different scaffolds and electronic structures.

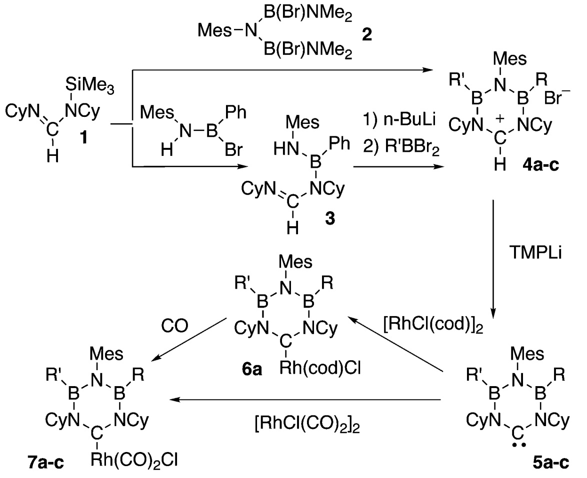
Borazines **G**, discovered by Stock[10] in 1926, and currently used for the fabrication of advanced material based on boron nitride,[11] constitute a family of extremely stable heterocycles. Because they are isoelectronic to benzene, they are often regarded as the archetypical example of an inorganic aromatic compound, although the extent of aromaticity of **G** in relation to that of benzene is still debated.[12] Since boranes are isoelectronic with both carbocations and carbenes, it was reasonable to believe that the mixed organic/inorganic heterocycles **H** and **I** would be quite stable. Importantly, the lone pairs of the nitrogen atoms, adjacent to the carbene center of **I**, can interact both with the carbene and with the boron vacant orbitals. Varying the nature of the substituents at the boron centers, and thus modifying their Lewis acidity, should allow for the preparation of carbenes with quasi-identical steric demands, but different electronic properties; this would permit a better understanding of the factors governing the catalytic activity of the ensuing complexes.

Derivative **4a**[13] was obtained in one step (83% yield) by treatment of N-silylated formamidine **1** with compound **2**. To replace the amino group at the boron centers by a weaker π-donor substituent, a different synthetic approach has been designed; indeed, 1,3-dibromo-1,3-diboranes of type **2** are only readily available with amino substituents. Derivative **3** was prepared according to a known procedure.[14] Then, deprotonation with *n*-butyllithium and subsequent treatment with the desired dibromoborane afforded derivatives **4b**,**c**[13] in 74 and 71% yield, respectively. The influence of the nature of the boron substituents is clearly apparent in the ^{1}H NMR chemical shift of the iminium proton: 8.8 (**4a**), 9.4 (**4b**), 9.7 (**4c**) ppm. Addition at −78 °C of lithium tetramethyl piperidine to a THF solution of derivatives **4a**−**c** cleanly afforded carbenes **5a**−**c**, which were isolated after recrystallization from hexanes as light-yellow crystals[13] (Scheme 2).

Scheme 1



Scheme 2



4a-**7a**: R = R' = NMe_2; **4b**-**7b**: R = Ph, R' = NMe_2; **4c**-**7c**: R = R' = Ph

Both types of heterocycles **4** and **5** are perfectly stable at room temperature, in solution, and in the solid state. The single-crystal X-ray diffraction study[15] of **4c** and **5c** (Figure 1) reveals, in both cases, the expected planar six-membered ring skeleton with a propeller-like arrangement of substituents. The cyclohexyl rings feature the most protecting conformation for the electron-deficient carbon center. As always observed, when comparing the geometric parameters of NHCs and those of their NHC(H+) precursors, the N2−C1−N3 angle for carbene **5c** (114.5°) is more acute than that for cation **4c** (122.8°). For the cation **4c**, the rather short endocyclic N−C distances (1.33 and 1.32 Å) and the somewhat longer N2−B1 and N3−B2 bond distances (1.46 and 1.47 Å) compared to those of B1−N1 and B2−N1 (1.42 and 1.43 Å) suggest that the nitrogen lone pairs interact primarily with the carbon center. Indeed, in borazines, B−N distances are in the range of 1.42−1.44 Å.[16] In other words, the six π-electrons are divided into two separated allyl moieties: a cationic four π-electron NCN and a neutral four π-electron BNB system. In contrast, carbene **5c** exhibits five B−N

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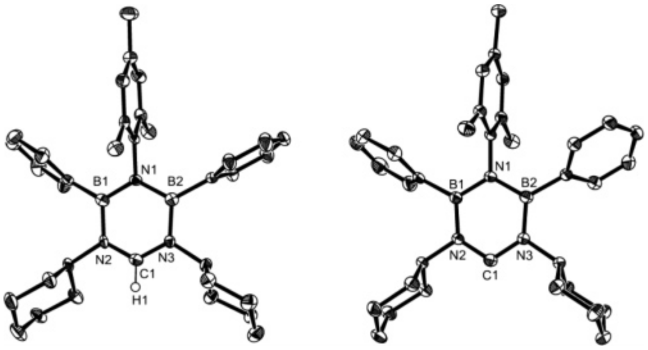

Figure 1. Thermal ellipsoid diagram (50% probability) of **4c** (left) and **5c** (right) (H atoms are omitted). Selected bond distances (Å) and angles (°): **4c** C1−N2 1.323(4), C1−N3 1.328(4), N2−B1 1.467(4), N3−B2 1.460(4), B1−N1 1.428(5), B2−N1 1.422(5), N2−C1−N3 122.8(3); **5c** C1−N2 1.3664(18), C1−N3 1.3634(18), N2−B1 1.4442(19), N3−B2 1.4449(19), B1−N1 1.4278(19), B2−N1 1.4356(19), N2−C1−N3 114.45(12).

bond lengths, which are about equal (1.43−1.44 Å), and relatively long CN bond distances (1.36−1.37 Å), indicating a more delocalized π-system.

To test the coordination ability of derivatives **5**, carbene **5c** was treated at −78 °C with half an equivalent of bis(μ-chlorocyclooctadienerhodium). After workup, complex **6c** was isolated as highly thermally stable single crystals. Not surprisingly, the value of the $C_{carbene}$−Rh bond length for **6c** (2.05 Å) is within the typical range for analogous complexes bearing classical NHC ligands **A**−**D** (2.00−2.06 Å).[17] To compare the electron-donating ability of carbenes **5a**−**c**, the corresponding *cis*-[RhCl(CO)$_2$(**5**)] complexes **7a**−**c** were prepared by treatment of **6c** with CO at room temperature, or alternatively by addition of carbenes **5a**−**c** to half an equivalent of bis(μ-chlorodicarbonylrhodium). The average value of the carbonyl stretching frequencies [ν_{av}(CO): 2029 (**7a**), 2033 (**7b**), 2038 (**7c**), cm^{-1}] clearly indicate that the donor power of carbenes **7** decreases in the order **7a** > **7b** > **7c**, following the donor ability of the boron substituents. It is important to note that (i) a difference of only 3 cm^{-1} was observed between the ν_{av}(CO) values of saturated **A** (2038) and unsaturated **B** (2041) NHCs; (ii) the donor power of **7a** and **7b** seems to be higher than those of **A** and **B**, which is in agreement with the higher electropositivity of boron compared to that of carbon.

In conclusion, carbene analogues of borazines are readily available as highly thermally stable species [mp 176 °C without decomposition (**7c**)]. They give rise to stable transition metal complexes. Importantly, their electronic properties can readily be tuned by varying the nature of the boron substituents. Their efficiency as organic catalysts and as ligands for transition metal catalysts is currently under investigation.

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Acknowledgment. Full experimental and spectroscopic data for all new compounds, and X-ray crystallographic data for **4c**, **5c**, and **6c** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Selected spectroscopic data: ^{13}C{^{1}H} δ 165.0 (**4a**), 165.0 (**4b**), 163.6 (**4c**), 282.9 (**5a**), 281.5 (**5b**), 281.6 (**5c**), 242.1 (J = 47.4 Hz) (**6c**), 242.1 (J = 47.4 Hz) (**7a**), 223.1 (J = 38.2 Hz) (**7b**), 224.3 (J = 38.6 Hz) (**7c**), [NCN]; ^{11}B{^{1}H} δ 25 (**4a**), 26 and 33 (**4b**), 35 (**4c**), 24 (**5a**), 24 and 31 (**5b**), 31 (**5c**), 32 (**6c**), 24 (**7a**), 25 and 32 (**7b**), 30 (**7c**); IR (CH_2Cl_2) ν 2069 and 1989 (**7a**), 2073 and 1994 (**7b**), 2077 and 2000 (**7c**) cm^{-1} [ν(CO)].
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